# Chesapeake Bay Program Mainstem Coordinated Split Sample Program Report

## May 2001 to May 2002

**January, 2003**

Chesapeake Bay Program
A Watershed Partnership

## Acknowledgments

This report was prepared by Mary Ellen Ley and Dave Jasinski of the Chesapeake Bay Program, with assistance from Carolyn Keefe of the University of Maryland Chesapeake Biological Laboratory. The report was reviewed and approved for release on the Chesapeake Bay Program Quality Assurance Website by the Analytical Methods and Quality Assurance Workgroup.

# Mainstem Split Sample Report – May 2001 to May 2002

## BACKGROUND

The Chesapeake Bay Coordinated Split Sample Program (CSSP) is an ongoing, inter-laboratory performance assessment that compares analytical results from different laboratories on identical environmental samples. This report assesses the comparability of laboratories monitoring the mainstem Chesapeake Bay. Five quarters of data are examined for the period May 2001 through May 2002, during which the following laboratories participated in the program:

- Old Dominion University (ODU)
- Chesapeake Biological Laboratory (CBL)
- Virginia Department of Consolidated Laboratory Services (DCLS)
- Maryland Department of Health and Mental Hygiene (DHMH)
- Academy of Natural Sciences and Estuarine Research (ANS) – Chlorophyll only.

Two laboratories, ODU and CBL, produce the majority of nutrient and sediment data for the mainstem monitoring program, however, the additional data provided by DCLS and DHMH give a better sense of a parameter's "true" value.

## PARAMETERS AND METHODS

Split samples are collected quarterly, distributed to participating laboratories, and analyzed for the following parameters:

| | |
|---|---|
| Total Dissolved Nitrogen (TDN) | Total Dissolved Phosphorus (TDP) |
| Particulate Nitrogen (PN) | Phosphate ($PO_4$) |
| Nitrate + Nitrite ($NO_{23}$) | Particulate Phosphorus (PP) |
| Nitrite ($NO_2$) | Particulate Carbon (PC) |
| Total Suspended Solids (TSS) | Ammonia ($NH_4$) |
| Chlorophyll *a* | Volatile Suspended Solids (VSS) |
| Silica (Si) | |

Split sample collection and handling procedures are documented on the Chesapeake Bay Program Website at:
http://www.chesapeakebay.net/pubs/quality_assurance/doc-cssp-procedures.pdf
A detailed comparison of laboratory methods can be found on the Chesapeake Bay Program website at:
http://www.chesapeakebay.net/pubs/quality_assurance/doc-Tidalmethodmtrx99wpd.pdf

Laboratories use identical methods for analyzing ammonia, nitrate, nitrite and orthophosphate. ODU, CBL and DCLS analyze total dissolved and particulate fractions of nitrogen and phosphorus directly, and calculate total nitrogen and phosphorus (TN & TP) from the sums. DHMH analyzes total and dissolved Kjeldahl nitrogen, from which PN is calculated by difference. DHMH analyzes total and dissolved phosphorus and calculates particulate phosphorus by difference. Calculating these parameters by difference often causes large discrepancies between DHMH and other laboratories in the split sample analyses, but because only CBL and ODU analyze Chesapeake Bay routine mainstem samples, discrepancies in the database would not be expected.

ODU, CBL and DCLS analyze particulate carbon (PC) directly, while DHMH analyzes TOC and DOC, and calculates PC by difference. Again, these calculations of PC only affect comparisons of split sample results and not the routinely collected mainstem data. For suspended solids and silica, laboratories use identical methods. For chlorophyll, the three laboratories routinely reporting mainstem chlorophyll data use a spectrophotometric method.

## GRAPHICAL ANALYSIS OF RESULTS

Graphs of the split sample results show which labs had results that are farther apart than their own laboratory precision estimates. Graphs of the means for each sample date for each lab are plotted showing this within-laboratory precision as "error bars". Any pair of lab means that do not have overlapping "error bars" have differences that were larger than their within-laboratory precision. The within-laboratory precision estimates for CSSP analysis are either 1) the standard error of the four sub-samples for each sample date; or 2) Twice the standard error of the difference between the certified and observed value the lab obtains when analyzing standard reference material (SRM) for the variable in question. Laboratory Method Limits (3.18 x MDL) are displayed on the graphs to put the reported concentrations into perspective with the lab's detection capability.

### PROBLEM IDENTIFICATION AND CORRECTIVE ACTION

Each quarter, results are plotted and reviewed for reporting errors by lab staff. Agreement among laboratories is examined quarterly at Analytical Methods and Quality Assurance Workgroup meetings. When there is poor agreement, the group discusses potential causes of problems and recommends investigative and corrective actions. On some occasions no potential cause for a consistent small bias is found despite careful assessments of potential causes and experimental investigations. This historical documentation of consistent bias thus serves as a tool for data users to appraise apparently small differences in concentration that may be due to inter-laboratory differences rather than environmental conditions.

A summary of the results, problems, corrective actions recommended and taken from May 2001 to May 2002 is given in Table 1. Parameters that consistently agree well include chlorophyll, nitrate, and silica. For laboratories using the same methods, there is good agreement for TDN, TDP, PN, and PC.

Ammonia, nitrite and phosphate have occasional agreement problems. The spread among TSS results appears to be widening; particulate phosphorus had agreement problems in 2001 that appear to be resolved in 2002.

### SUPPORTING QC DATA

Standard reference material results and spike recovery data for mainstem CSSP samples collected from May 2001 to May 2002 are given in Table 2. Laboratories analyze laboratory spiked samples and standard reference materials (SRM) to aid in data interpretation and problem identification. These QC results are indicators of bias associated with a particular analytical system. Consistent, low recoveries (e.g., < 90%) on spike and SRM samples suggest that the data are biased low, while recoveries > 110% suggest that the results may be biased high. Different patterns of bias between the SRM and spiked samples may indicate matrix effects from the sample.

### SUMMARY OF LABORATORY CORRECTIVE ACTIONS

**CBL** - Identified sources of field sub-sampling contamination for ammonium, nitrate, nitrite and phosphate in regular mainstem cruises commencing 5/28/01. SRM data need to be reprinted for PN, PC, PP, and silica.

**DCLS** – Silica samples will be reported as $SiO_2$. Sources of contamination for ammonium and PP were investigated, and steps taken for preventing future contamination. SRMs are needed for PN, PC, and PP.

**DHMH** – Need to identify cause of high $NH_4$ results and analyze split samples for VSS. AMQAW will discontinue comparing this lab's PC and PN results since they are calculated parameters.

**ODU** – Need to monitor PN bias – Acquire SRM for PN.

**ANS** – Report chlorophyll split sample results directly to Dave Jasinski according to CSSP schedule.

**Table 1. Laboratory Performance on Mainstem Coordinated Split Samples - May 2001 to May 2002**

Note: Click the parameter in the left column to access the associated graph

| Nitrogen Species | Status / Problem | Possible Causes and Recommended Actions | Outcome and Resolution |
|---|---|---|---|
| **Total Dissolved Nitrogen (TDN)**<br>**Colorimetric with:**<br>Alk. Persulfate Digestion (CBL, ODU, DCLS)<br>Calculated: DKN + $NO_{23}$ (DHMH) | Results agree well among ODU, CBL and DCLS, who use the same method. The range of results on all but one sampling date is small. All values are at or above the lowest calibration standard; none of the labs had a coefficient of variation (CV) > 25% among their replicates. Concurrent spike recoveries were excellent. DHMH results are 50% lower than others in Aug. 01. | Unknown cause of DHMH low value – Good agreement in Feb. 02, but biased high 8/02 and 11/02. | Differences possibly due to DHMH use of Kjeldahl method. Method change may be recommended in the future. |
| **Particulate Nitrogen (PN)**<br>Combustion/Oxidation (CBL, ODU, DCLS)<br>Calculated: TKN-DKN (DHMH) | Particulate nitrogen results agree fairly well among ODU, CBL and DCLS, who use the same method. Concurrent SRM recoveries were not reported. The range among labs seems to be narrowing, however, ODU has developed a slight negative bias relative to CBL and DCLS since Aug. 2001.<br><br>DHMH results are biased low in May 2001and Feb. 2002. | ODU low bias may coincide with the purchase of a new instrument.<br><br>DHMH calculates PN, which is likely cause of negative bias. Comparing calculated PN to directly measured PN is inappropriate. Include a lab that analyzes PN directly. | Labs to analyze and report PN SRM.<br><br>VIMS analyzes PN directly and will participate in the mainstem CSSP beginning Nov. 2002. DHMH data will no longer be used for this comparison. |
| **Ammonium Nitrogen ($NH_4$ F)**<br>Colorimetric, Indophenol<br>(all labs) | Results do not always agree well among the four labs, although they use the same method, and concentrations are above MLs. ODU and DCLS have good agreement, while DHMH and CBL often have much higher results relative to the other labs. Both appear biased high in Aug. 2001. DHMH continues to be high through Feb. 2002; CBL results are high again in May 2002.<br><br>CBL and ODU have 3 CVs > 25% among three of the split sample replicates. Concurrent spike and commercially prepared SRM sample recoveries were excellent. | DCLS did not report data for the Feb. 2002 split because of contamination.<br><br>Contamination of AA cups filled in field likely cause of CBL high bias and variability among replicates.<br><br>DHMH high results may be due to not using artificial seawater in calibration standards.<br><br>ODU to investigate reason for CVs > 25%. | DCLS is uncertain if samples contaminated in field or lab. To prevent lab contamination, associated glassware will be washed after use and again immediately prior to use.<br><br>MDNR field staff reviewed sampling & handling procedures July-Aug. 2001.<br><br>DHMH use of artificial seawater did not resolve problem<br><br>ODU reps 3 &4 were run with higher calibrants. Aug & Nov 02 samples OK. |
| **Nitrite Nitrogen (NO2F)**<br>**Colorimetric, (all labs)** | CBL is biased high relative to other labs, who agree well with each other. Need to identify problem and take corrective action. | Contamination of AA cups filled in field likely cause of CBL high bias and variability among replicates. | In July and Aug. 2001, MDNR field staff reviewed proper handling of sample containers. |
| **Nitrate + Nitrite Nitrogen (NO23F)**<br>Colorimetric, Cadmium Reduction<br>**(all labs)** | Nitrate + nitrite results have good agreement, even at concentrations near method limits. May 2001 results (off scale of graph) ranged from 0.272 to 0.337 mg/L.<br>CBL's Aug. 2001 result is several times higher than other labs; the range of replicates on this date was high (0.0046 to 0.029 mg/L). Results agree better in next 3 quarters. | Dave J. to check spreadsheet calculations. Incorrect values plotted for CBL for Aug 01& May 02. Correct values are 0.014 & 0.070.<br><br>Contamination of AA cups filled in field likely cause of CBL bias and variability among replicates. | In July and Aug. 2001, MDNR field staff reviewed proper handling of sample containers. |

**Table 1.** *(Cont'd)* **LABORATORY PERFORMANCE ON MAINSTEM COORDINATED SPLIT SAMPLES - May 2001 to May 2002**

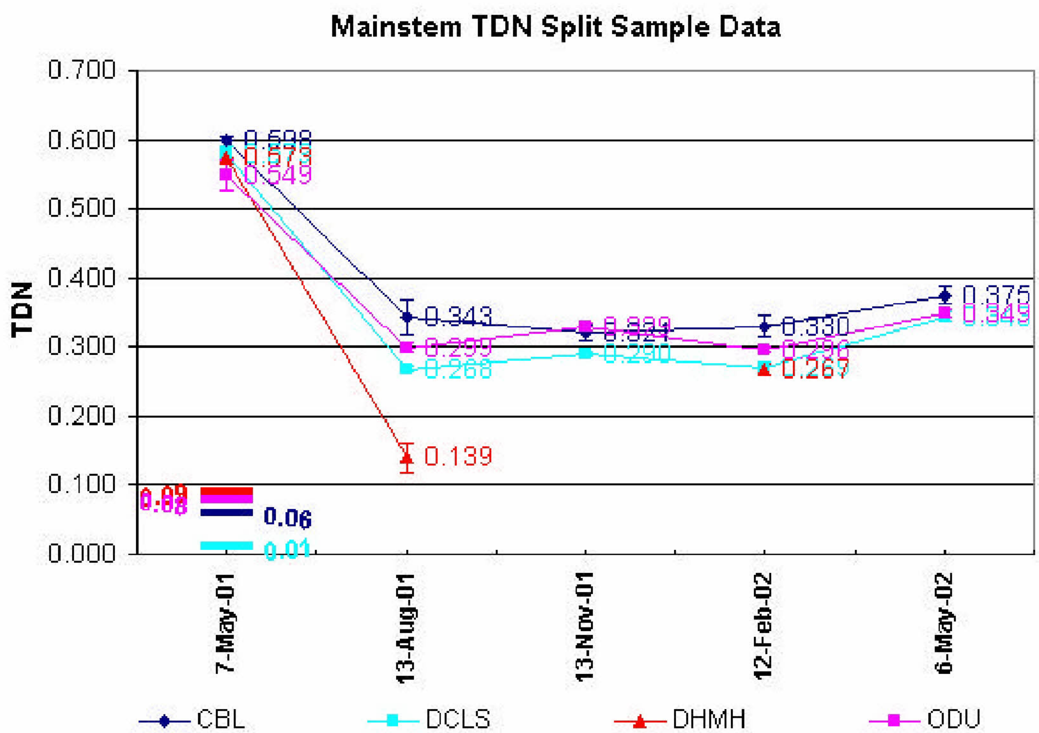
**Note:** Click the parameter in the left column to access the associated graph

| Phosphorus Species | Status / Problem | Possible Causes and Recommended Actions | Outcome and Resolution |
|---|---|---|---|
| **Total Dissolved Phosphorus (TDP)**<br>**Colorimetric with:**<br>Alk. Persulfate Digestion (CBL, ODU, DCLS)<br><br>TKN Digestion (DHMH) | Good agreement among labs, except DHMH biased high May - Aug. 2001 and May 2002. DHMH values are at or below their method limit of 0.03 mg/L,which is 10 times higher than other laboratory MLs.<br><br>Within lab replication is good on all dates for all labs. Slightly low spike recoveries occur for all except CBL.<br><br>ODU continues a slight negative bias relative to other labs | DHMH uses a Kjeldahl digestion, which does not appear to be sensitive enough for these low levels.<br><br>CBL has investigated low bias of ODU relative to CBL in the past but no statistically significant bias was documented. | No DHMH action necessary because routine data not produced. |
| **Particulate Phosphorus (PP)**<br>Colorimetric with Acid Digestion (CBL, ODU, DCLS)<br><br>Calculated: TP-TDP (DHMH) | ODU and CBL have excellent agreement. DHMH agrees well even though PP is calculated.<br><br>DCLS is biased high in May, Aug. and Nov. 2001 but not in Feb. 2002. Data from May 2002 were not reported<br><br>CBL and DCLS did not report PP SRM results. | Comparing DHMH calculated PP to directly measured PP is inappropriate. It would be better to include a lab that analyzes PP directly.<br><br>DCLS uses an aqueous PP SRM so not a "true" SRM. Check sources of PP SRM.<br><br>DCLS May 2002 sample was contaminated. The Aug. 2002 results are important to see if better agreement. | VIMS analyzes PP directly and will participate in the mainstem CSSP beginning Nov. 2002. DHMH data will no longer be used for this comparison.<br><br>CBL will report SRM results for PP.<br><br>DCLS had contaminated HCL, which was replaced by higher grade. Will run blank when lot number changes to ensure clean. (The Aug. and Dec. 02 samples still biased high.) |
| **Orthophosphate (PO4F)**<br>**Colorimetric (all labs)** | There is fair agreement among laboratories considering that concentrations are low on all dates, very close to laboratory method limits. Notes:<br>• CBL results relatively high in Aug. 2001, subsequently in closer agreement. This pattern also occurs with $NO_3$.<br><br>• ODU negatively biased relative to other labs.<br><br>• DCLS positively biased relative to other labs. | Contamination of AA cups filled in field likely cause of CBL high bias.<br><br>Past investigations have not determined cause of ODU negative bias.<br><br>DCLS ML is higher than other labs, but is appropriate for tributary samples. Lower concentrations atypical for this lab, so not affecting data quality. | In July and Aug. 2001, MDNR field staff reviewed proper handling of sample containers.<br><br>No further ODU action at this time.<br><br>DCLS differences at low level are due to using the y-intercept in the regression calculations to calculate data values. Other labs calibrate with a zero standard or force the calibration curve through zero. The method does not prescribe calibration standards, sod is determined by the laboratory. |

**TABLE 1.** ***(Cont'd)*** **LABORATORY PERFORMANCE ON MAINSTEM COORDINATED SPLIT SAMPLES - May 2001 to May 2002**
Note: Click the parameter in the left column to access the associated graph

| Carbon, Solids, Chlorophyll, Silica | Status / Problem | Possible Causes and Recommended Actions | Outcome and Resolution |
|---|---|---|---|
| **Chlorophyll *a***<br>Spectrophotometric (DCLS, ODU, DHMH, ANS)<br><br>Fluorometric (CBL) | Results agree well among all laboratories for all dates. Only CBL has a slight consistent high bias relative to other results<br><br>ANS submitted data for 3/5 quarters, results appear to be biased low. | Fluorometric technique may cause slight bias, however, CBL does not analyze routine samples for mainstem Chesapeake.<br><br>ANS to review chlorophyll procedure. | None necessary for CBL. |
| **Total Suspended Solids (TSS)**<br><br>Gravimetric (All labs) | The range of TSS results among labs is widening. In May 2002, results ranged from 2.5 to 7.1 mg/L TSS.<br><br>ODU is consistently the highest value and DCLS the lowest value on most dates. Within lab precision is good. | May be due to differences in sub-sampling technique. Recommend filling graduated cylinder quickly to avoid solids settling in sample container. | See if results improve in 2003. |
| **Volatile Suspended Solids (VSS)**<br>Gravimetric (All labs) | VSS results are plotted for DCLS and CBL, but FSS are plotted separately for ODU.<br><br>DHMH has neither VSS nor FSS plotted. | Need to calculate all laboratories' VSS and plot only VSS results (FSS unnecessary).<br><br>DHMH needs to analyze VSS for CSSP. | DHMH to analyze VSS split samples beginning in Nov 02. |
| **Particulate Carbon (PC)**<br>Combustion/Oxidation (CBL, ODU, DCLS)<br>Calculated: TOC-DOC (DHMH) | Results agree well among ODU, CBL and DCLS, who use the same method. They are biased relative to each other, with ODU always the lowest and DCLS the highest of the 3 labs.<br><br>CBL and DCLS did not report PC SRM results<br><br>DHMH results are much lower than the other labs. Feb. and May 2002 are not plotted. | DHMH low bias due to particulate TOC settling out during analyses, thus underestimating TOC. Comparing calculated PC to directly measured PC is inappropriate. It would be better to include a lab that analyzes PC directly.<br><br>DHMH May 2002 sample had DOC >TOC. | VIMS analyzes PC directly and will participate in the mainstem CSSP beginning Nov. 2002. DHMH data will no longer be used for the PC comparison.<br><br>CBL and DCLS will analyze and report PC SRM results. |
| **Silica**<br>Colorimetric (All labs) | Excellent agreement among laboratories, except for Feb. and May 2002, where DCLS results were 2-3 times higher than others. | DCLS reported concentrations of $SiO_2$ instead of Si. Results will be recalculated and resubmitted. | DCLS split samples will be reported as Si as of Aug. 02. |

Mary Ellen Ley
January 22, 2003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TDN
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0.600
0.500
0.400
0.300
0.200
0.100
0.000
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0.573
0.549
0.343
0.299
0.268
0.139
0.330
0.267
0.375
0.349
0.06
0.01
7-May-01
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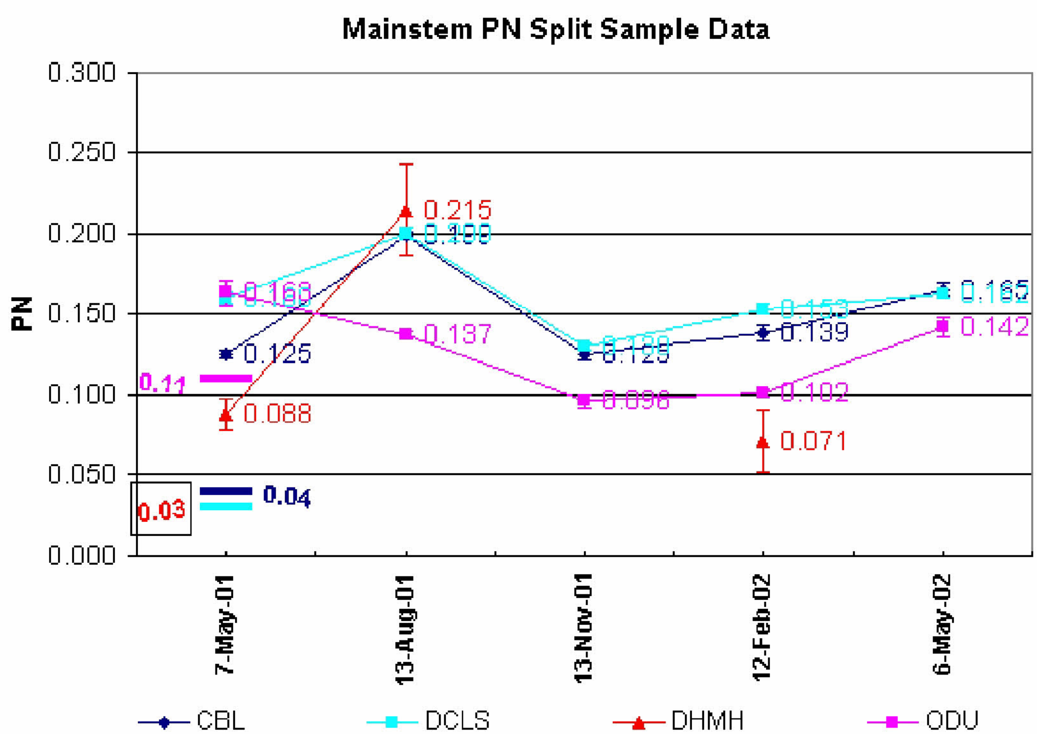
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem PN Split Sample Data
PN
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0.250
0.200
0.150
0.100
0.050
0.000
0.215
0.163
0.125
0.088
0.137
0.11
0.04
0.03
0.096
0.139
0.102
0.071
0.165
0.142
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU



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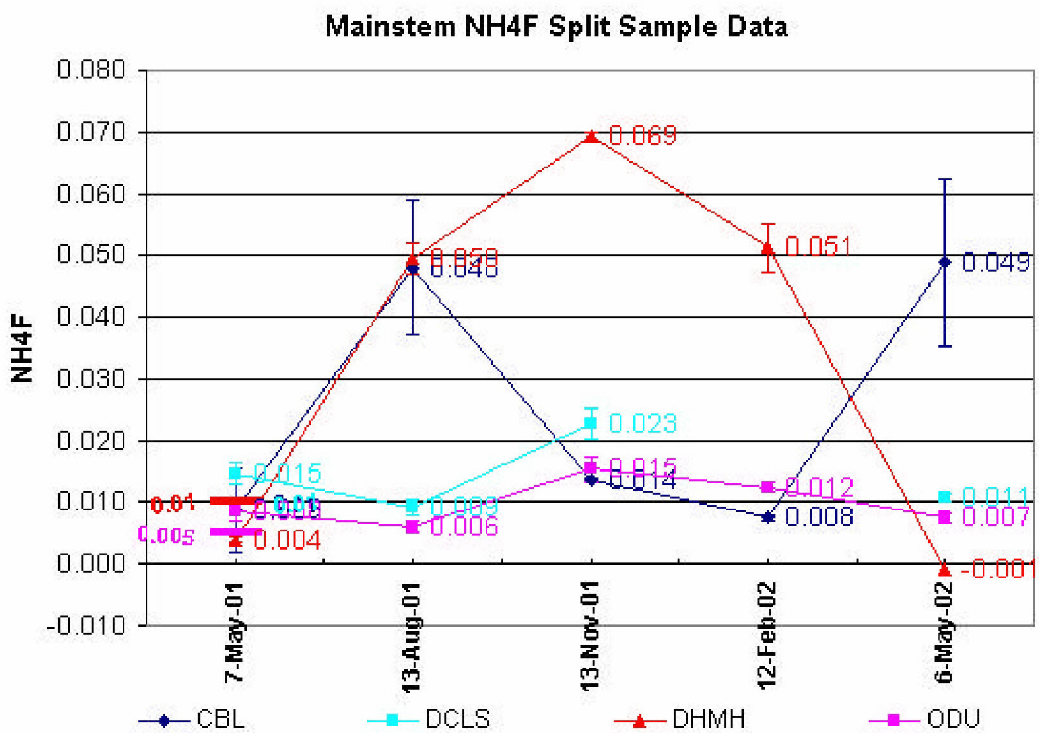

Mainstem NH4F Split Sample Data
NH4F
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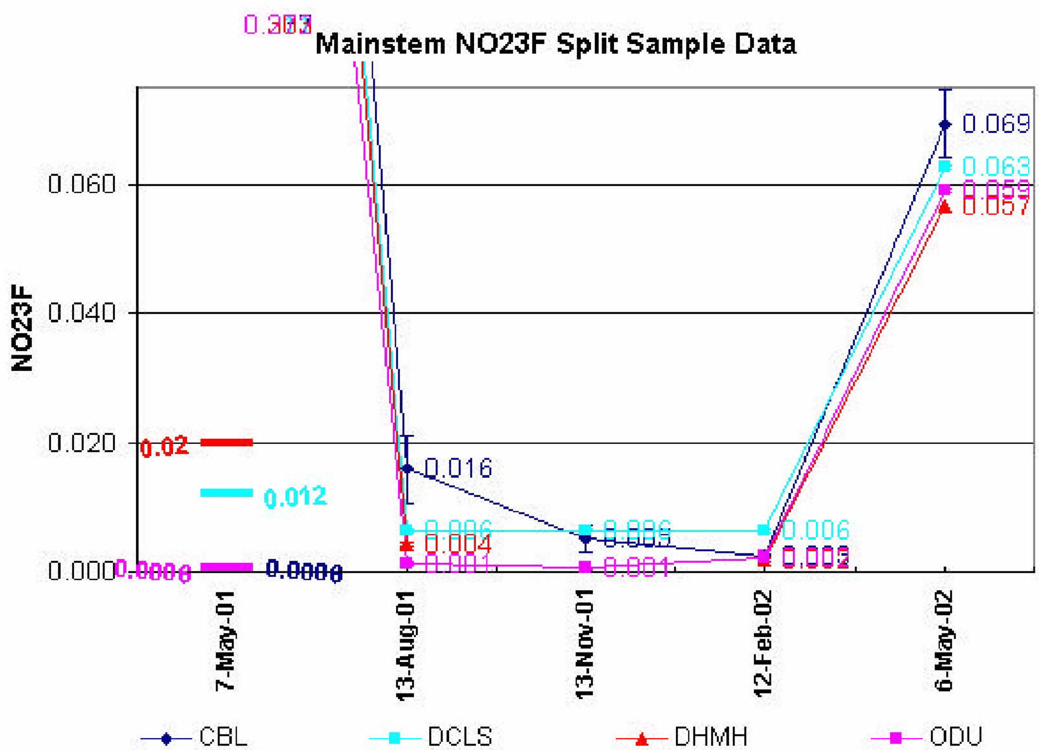
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
-0.010
0.069
0.051
0.049
0.048
0.023
0.015
0.015
0.014
0.012
0.011
0.009
0.008
0.007
0.006
0.004
-0.001
0.01
0.005
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU

Mainstem NO23F Split Sample Data
NO23F
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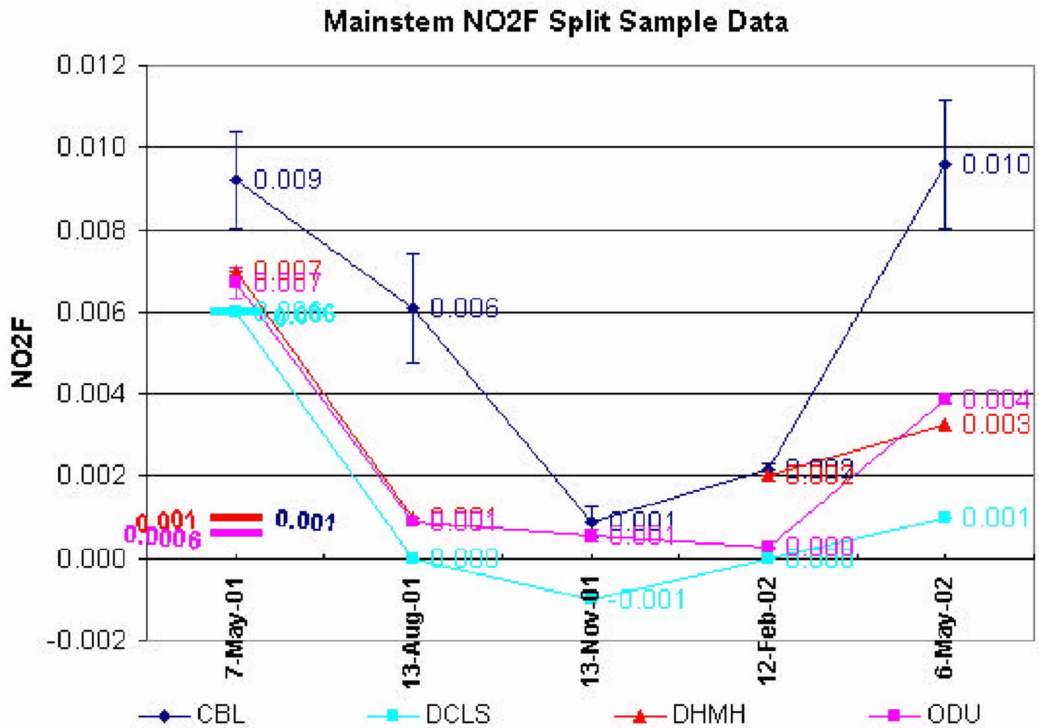
0.040
0.020
0.000
0.069
0.063
0.057
0.016
0.006
0.006
0.004
0.001
0.001
0.02
0.012
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU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NO2F
0.012
0.010
0.008
0.006
0.004
0.002
0.000
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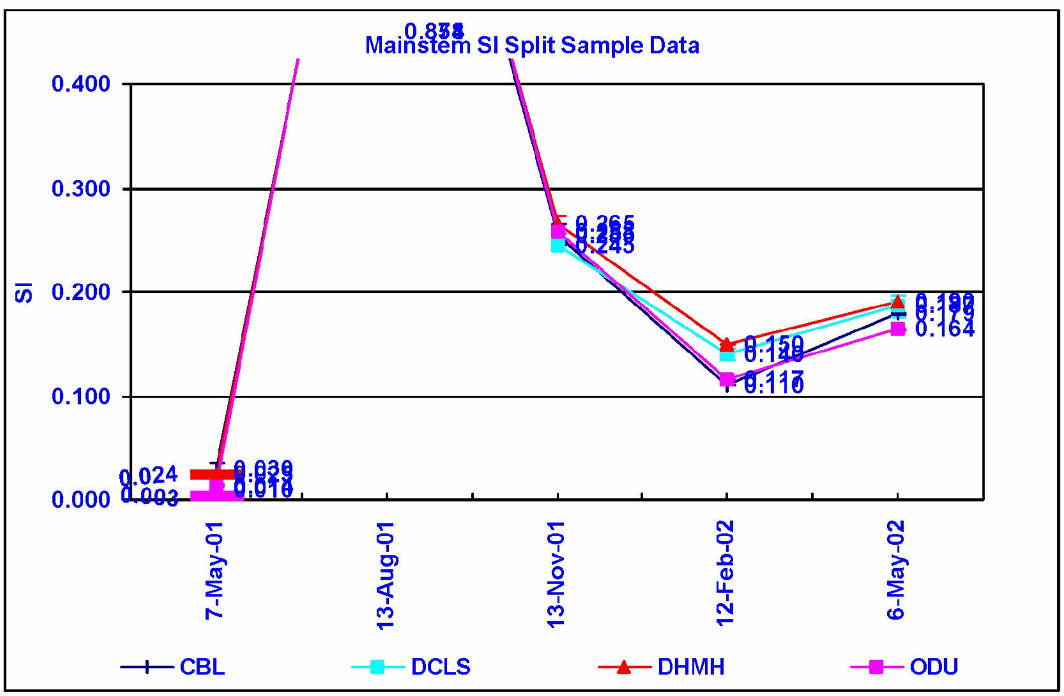
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU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SI
0.400
0.300
0.200
0.100
0.000
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13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU



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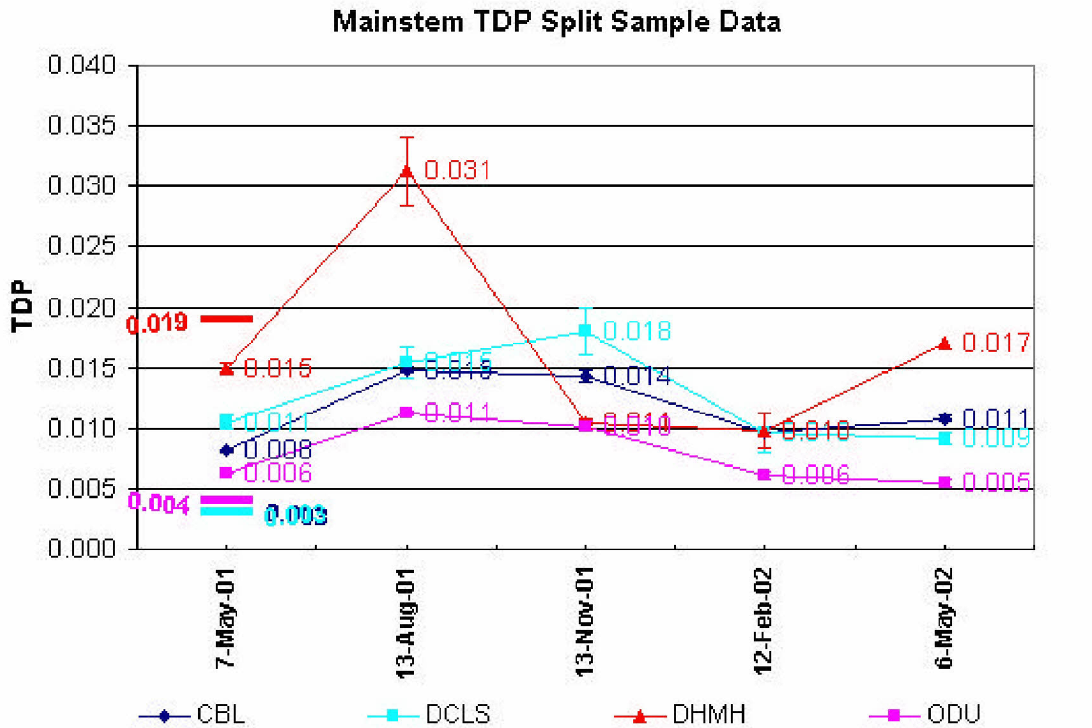
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TDP
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0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.031
0.019
0.018
0.017
0.015
0.014
0.011
0.008
0.006
0.005
0.004
0.003
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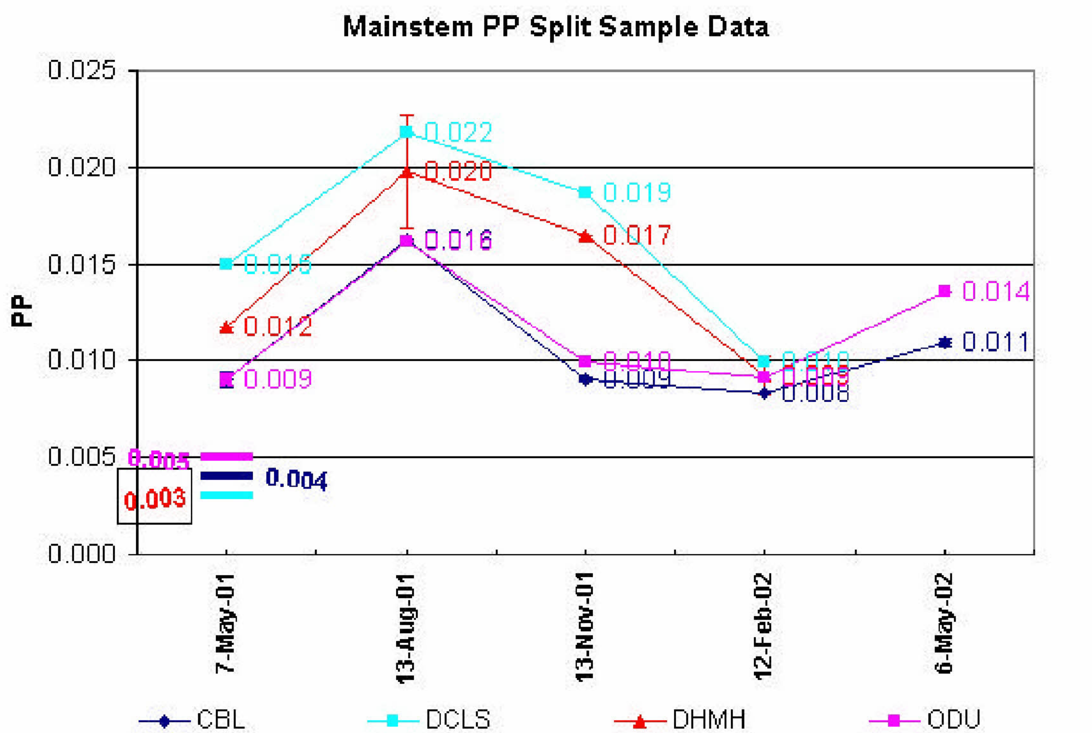
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem PP Split Sample Data
PP
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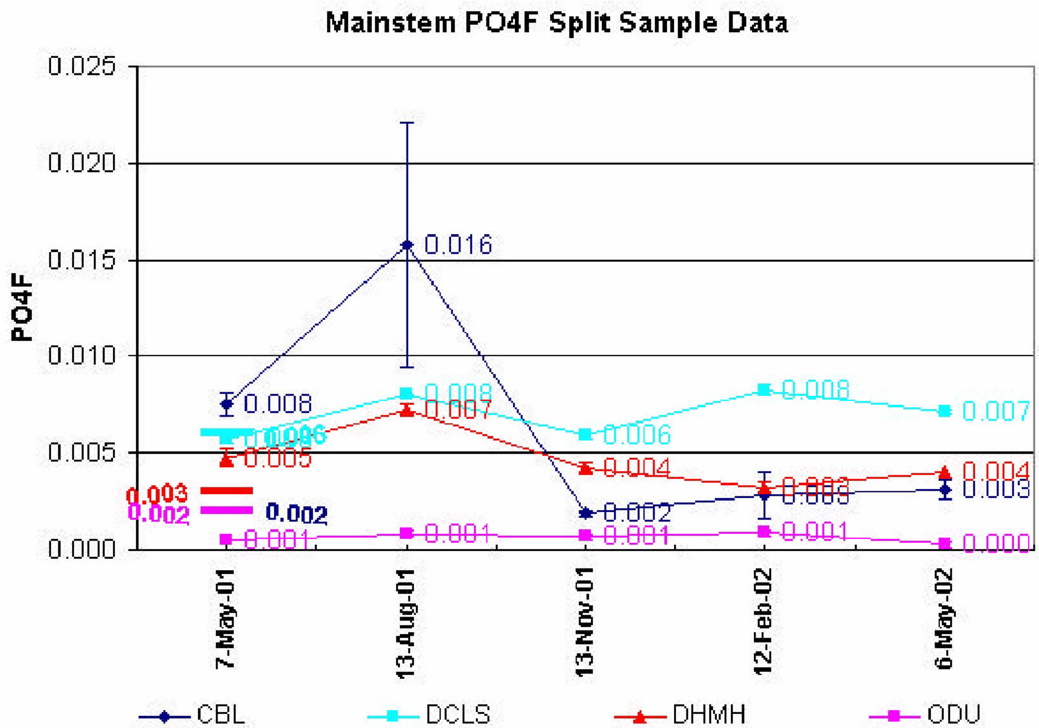
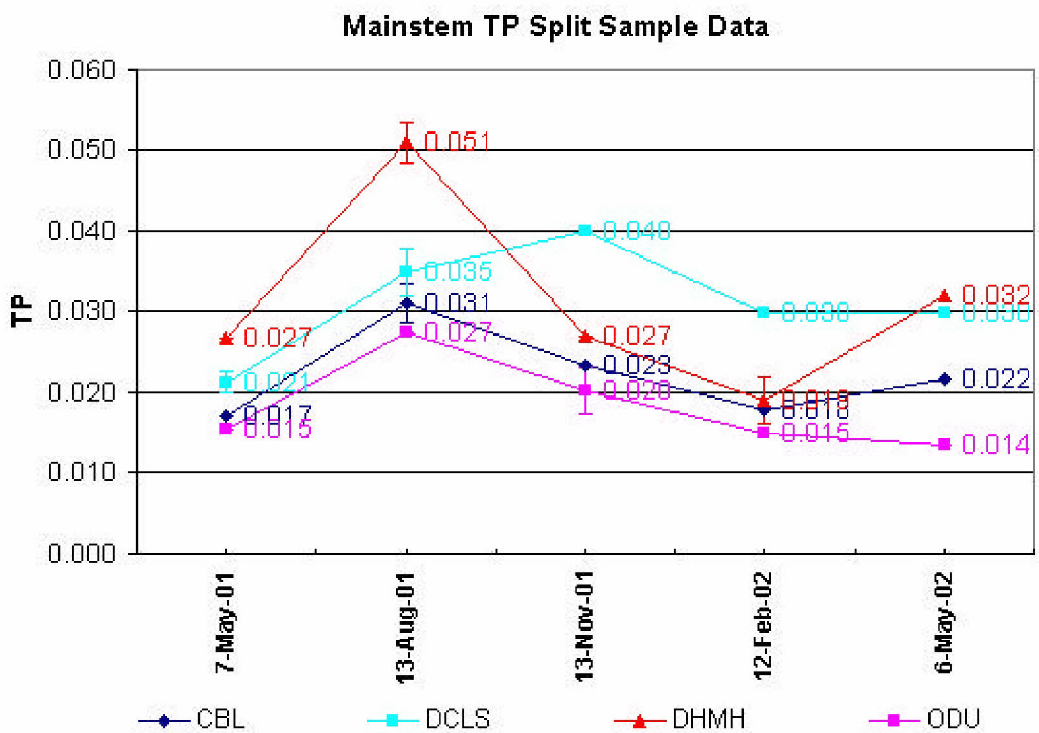
0.020
0.015
0.010
0.005
0.000
0.022
0.020
0.019
0.017
0.016
0.014
0.012
0.011
0.009
0.008
0.004
0.003
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem PO4F Split Sample Data
PO4F
0.025
0.020
0.015
0.010
0.005
0.000
0.016
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem TP Split Sample Data
TP
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0.051
0.040
0.035
0.032
0.031
0.027
0.022
0.021
0.017
0.015
0.014
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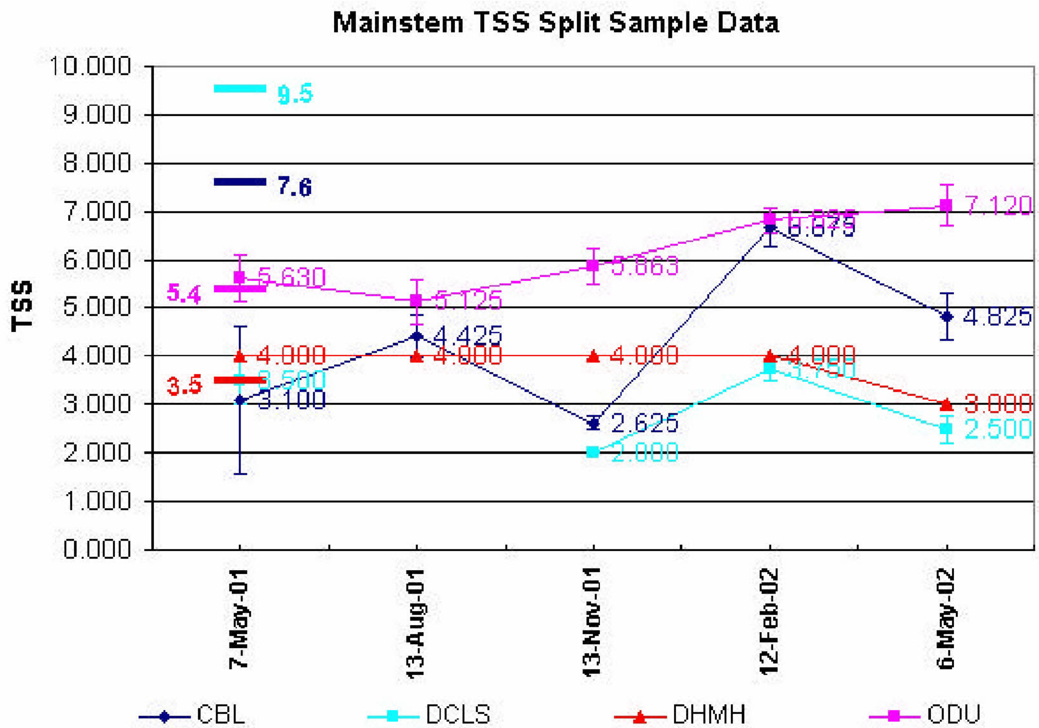
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem TSS Split Sample Data
TSS
10.000
9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
9.5
7.6
5.4
3.5
5.630
5.125
5.863
7.120
4.425
2.625
4.825
3.100
4.000
3.000
2.000
2.500
7-May-01
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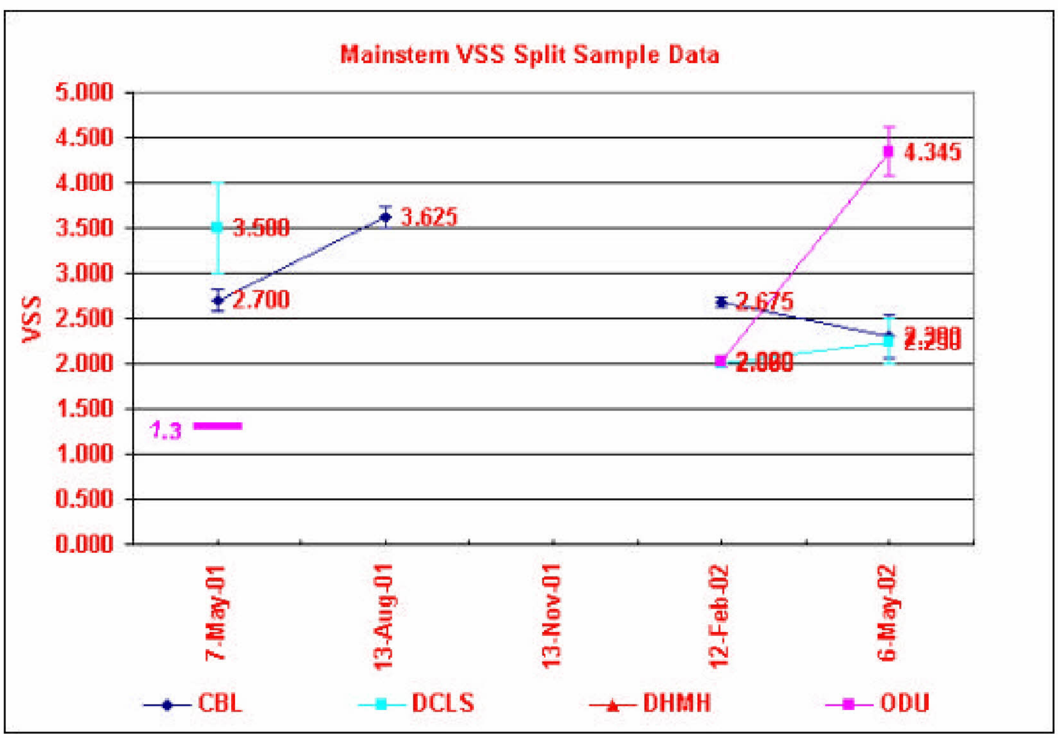
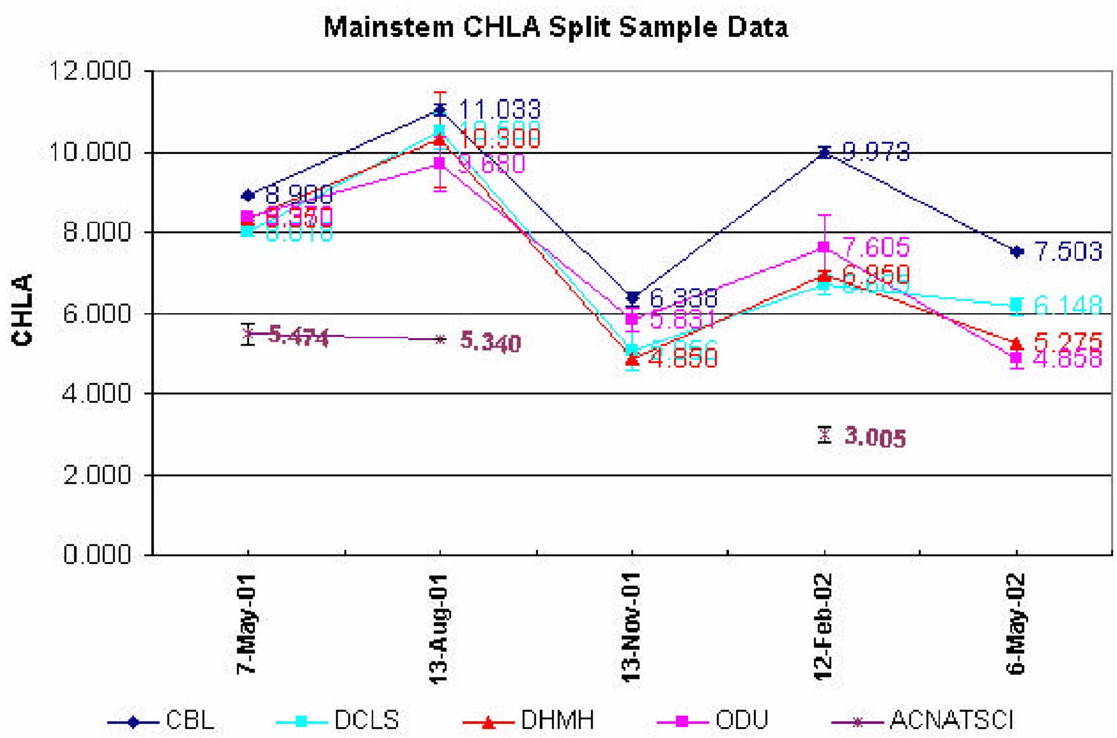
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU


Mainstem VSS Split Sample Data
VSS
5.000
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
4.345
3.500
3.625
2.700
2.675
1.3
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU



Mainstem CHLA Split Sample Data
CHLA
12.000
10.000
8.000
6.000
4.000
2.000
0.000
11.033
9.973
7.503
8.900
6.338
7.605
9.680
5.831
6.148
5.275
4.850
4.858
5.474
5.340
3.005
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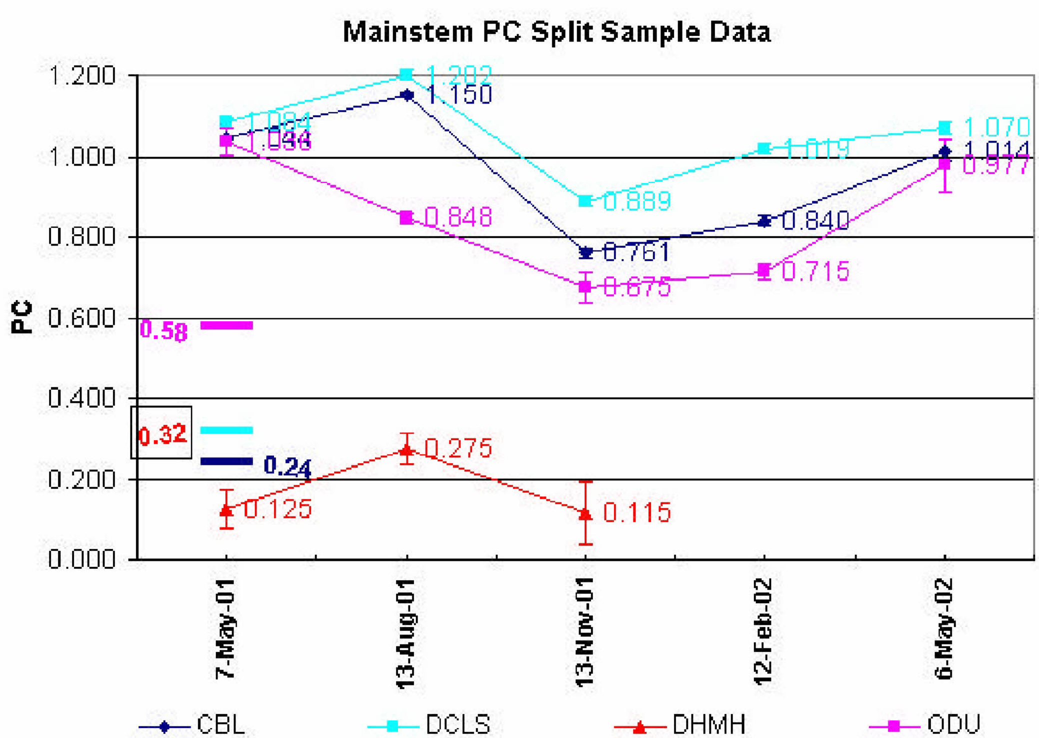
DHMH
ODU
ACNATSCI

Mainstem PC Split Sample Data
PC
1.200
1.000
0.800
0.600
0.400
0.200
0.000
1.150
1.070
1.014
0.977
0.848
0.889
0.840
0.761
0.675
0.715
0.58
0.32
0.24
0.275
0.125
0.115
7-May-01
13-Aug-01
13-Nov-01
12-Feb-02
6-May-02
CBL
DCLS
DHMH
ODU

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| Table 2. Standard Reference Material and Spike Recovery Data, May 2001 through May 2002 | | | | | | |
|---|---|---|---|---|---|---|
| **Parameter** | **Lab** | **Cruise Date** | **QC Type** | **Sub-samp** | **% SRM Recovery** | **% Spike Recovery** |
| **NH4F** | CBL | May-01 | SRM/SPK | 1 | 101 | 101 |
| | | May-01 | SRM/SPK | 3 | 104 | 90 |
| | | Aug-01 | SRM/SPK | 2 | 97 | 87 |
| | | Aug-01 | SRM/SPK | 3 | 93 | 84 |
| | | Nov-01 | SRM/SPK | 3 | 92 | 108 |
| | | Feb-02 | SRM/SPK | 4 | 99 | 92 |
| | | Feb-02 | SRM/SPK | 1 | 101 | 95 |
| | | May-02 | SRM/SPK | 1 | 102 | 95 |
| | | May-02 | SRM/SPK | 3 | 101 | 92 |
| **NH4F** | DCLS | May-01 | SRM/SPK | 4 | 106 | 102 |
| | | Aug-01 | SRM/SPK | 1 | 106 | 102 |
| | | Nov-01 | SRM/SPK | 4 | 108 | 100 |
| | | Feb-02 | SRM | ? | 106 | - |
| | | May-02 | SRM | ? | 103 | - |
| **NH4F** | DHMH | May-01 | SPK | 1 | - | 107 |
| | | Aug-01 | SPK | 1 | - | 107 |
| | | Nov-01 | SPK | 1 | - | 99 |
| | | Feb-02 | SPK | 1 | - | 116 |
| | | May-02 | SRM/SPK | 1 | 107 | 81 |
| **NH4F** | ODU | May-01 | SRM/SPK | 1 | 107 | 105 |
| | | May-01 | SRM/SPK | 1 | 101 | 104 |
| | | Aug-01 | SRM/SPK | 1 | 104 | 104 |
| | | Aug-01 | SRM/SPK | 1 | 96 | 100 |
| | | Nov-01 | SRM/SPK | 1 | 101 | 91 |
| | | Nov-01 | SRM/SPK | 1 | 106 | 103 |
| | | Feb-02 | SRM/SPK | 1 | 103 | 108 |
| | | Feb-02 | SRM/SPK | 1 | 102 | 100 |
| | | May-02 | SRM/SPK | 1 | 103 | 103 |
| | | May-02 | SRM/SPK | 1 | 100 | 107 |
| | | | | | | |
| **NO23F** | CBL | May-01 | SRM/SPK | 2 | 104 | 98 |
| | | May-01 | SRM/SPK | 4 | 101 | 95 |
| | | Aug-01 | SRM | 3 | 101 | - |
| | | Aug-01 | SRM | 4 | 103 | - |
| | | Nov-01 | SRM | 4 | 99 | - |
| | | Nov-01 | SRM/SPK | 1 | 96 | 103 |
| | | Feb-02 | SRM/SPK | 2 | 106 | 100 |
| | | Feb-02 | SRM/SPK | 4 | 111 | 101 |
| | | May-02 | SRM/SPK | 3 | 110 | 103 |
| | | May-02 | SRM/SPK | 4 | 112 | 109 |

| Table 2. (con't.) Standard Reference Material and Spike Recovery Data, May 2001 through May 2002 | | | | | | |
|---|---|---|---|---|---|---|
| **Parameter** | **Lab** | **Cruise Date** | **QC Type** | **Sub-samp** | **% SRM Recovery** | **% Spike Recovery** |
| **NO23F** | ODU | May-01 | SRM/SPK | 1 | 100% | 106% |
| | | May-01 | SRM/SPK | 1/3 | 100 | 99 |
| | | Aug-01 | SRM/SPK | 1 | 100 | 99 |
| | | Aug-01 | SRM/SPK | 1/3 | 103 | 99 |
| | | Nov-01 | SRM/SPK | 1 | 99 | 99 |
| | | Nov-01 | SRM/SPK | 1/3 | 101 | 101 |
| | | Feb-02 | SRM/SPK | 1 | 99 | 99 |
| | | Feb-02 | SRM/SPK | 1/3 | 101 | 98 |
| | | May-02 | SRM/SPK | 1 | 102 | 92 |
| | | May-02 | SRM/SPK | 1/3 | 102 | 93 |
| **NO23F** | DHMH | May-01 | SPK | 1 | - | 99 |
| | | Aug-01 | SPK | 1 | - | 101 |
| | | Nov-01 | SPK | 1 | - | - |
| | | Feb-02 | SPK | 1 | - | 100 |
| | | May-02 | SRM | 1 | 102 | - |
| | | May-02 | SRM | 1 | 102 | - |
| | | May-02 | SRM | 1 | 100 | - |
| | | May-02 | SRM | 1 | 101 | - |
| **NO23F** | DCLS | May-01 | SRM/SPK | 4 | 102 | 92 |
| | | Aug-01 | SRM/SPK | 1 | 100 | 92 |
| | | Nov-01 | SRM/SPK | 4 | 100 | 90 |
| | | Feb-02 | SRM/SPK | 4 | 98 | 100 |
| | | May-02 | SRM | ? | 103 | - |
| | | | | | | |
| **PC** | ODU | May-01 | SRM | 2 | 92 | - |
| | | May-01 | SRM | 1 | 108 | - |
| | | Aug-01 | SRM | 1 | 92 | - |
| | | Aug-01 | SRM | 1 | 93 | - |
| | | Nov-01 | SRM | 1 | 91 | - |
| | | Nov-01 | SRM | 1 | 92 | - |
| | | | | | | |
| **TDN** | CBL | May-01 | SPK | 3 | - | 94 |
| | | May-01 | SPK | 1 | - | 100 |
| | | Aug-01 | SRM/SPK | 2 | 106 | 100 |
| | | Aug-01 | SRM/SPK | 3 | 106 | - |
| | | Nov-01 | SRM/SPK | 2 | 102 | 104 |
| | | Nov-01 | SRM/SPK | 4 | 100 | 106 |
| | | Feb-02 | SRM/SPK | 1 | 95 | 100 |
| | | Feb-02 | SRM/SPK | 4 | 102 | 107 |
| | | May-02 | SRM/SPK | 1 | 95 | 100 |
| | | May-02 | SRM/SPK | 3 | 93 | 101 |
| | | May-02 | SPK | 2 | - | 98 |

| Table 2. (con't.) Standard Reference Material and Spike Recovery Data, May 2001 through May 2002 | | | | | | |
|---|---|---|---|---|---|---|
| **Parameter** | **Lab** | **Cruise Date** | **QC Type** | **Sub-samp** | **% SRM Recovery** | **% Spike Recovery** |
| **TDN** | DCLS | May-01 | SRM/SPK | 4 | 97% | 95% |
| | | Aug-01 | SRM/SPK | 4 | 98 | 103 |
| | | Nov-01 | SRM/SPK | ? | 103 | 98 |
| | | Feb-02 | SRM/SPK | ? | 101 | 109 |
| | | May-02 | SRM | ? | 102 | - |
| **TDN** | ODU | May-01 | SRM | 1 | 102 | 88 |
| | | May-01 | SRM | 1 | 98 | 93 |
| | | Aug-01 | SRM/SPK | 1 | 100 | 102 |
| | | Aug-01 | SRM/SPK | 1/3 | 98 | 116 |
| | | Nov-01 | SRM/SPK | 1/2 | 103 | 107 |
| | | Nov-01 | SRM/SPK | 1/4 | 101 | 114 |
| | | Feb-02 | SRM/SPK | 2/1 | 103 | 100 |
| | | Feb-02 | SRM/SPK | 3/1 | 105 | 96 |
| | | May-02 | SRM/SPK | 2/1 | 107 | 94 |
| | | May-02 | SRM/SPK | 3/1 | 109 | 100 |
| | | | | | | |
| **TDP** | CBL | May-01 | SPK | 3 | - | 94 |
| | | May-01 | SPK | 1 | - | 100 |
| | | Aug-01 | SRM/SPK | 2 | 96 | 105 |
| | | Aug-01 | SRM | 3 | 96 | - |
| | | Nov-01 | SRM/SPK | 2 | 100 | 100 |
| | | Nov-01 | SRM/SPK | 4 | 100 | 100 |
| | | Feb-02 | SRM/SPK | 1 | 109 | 100 |
| | | Feb-02 | SRM/SPK | 4 | 105 | 107 |
| | | May-02 | SRM/SPK | 2 | 104 | 102 |
| | | May-02 | SRM/SPK | 3 | 107 | 101 |
| **TDP** | DCLS | May-01 | SRM/SPK | 4 | 102 | 101 |
| | | Aug-01 | SRM/SPK | 4 | 106 | 100 |
| | | Nov-01 | SRM/SPK | ? | 98 | 92 |
| | | Feb-02 | SRM/SPK | ? | 106 | 97.3 |
| | | May-02 | SRM | ? | 100 | - |
| **TDP** | ODU | May-01 | SRM/SPK | 1 | 92 | 98 |
| | | May-01 | SRM/SPK | 1 | 91 | 93 |
| | | Aug-01 | SRM/SPK | 1 | 94 | 98 |
| | | Aug-01 | SRM/SPK | 1/3 | 95 | 103 |
| | | Nov-01 | SRM/SPK | 1/2 | 90 | 95 |
| | | Nov-01 | SRM/SPK | 1/4 | 89 | 100 |
| | | Feb-02 | SRM/SPK | 1 | 94 | 99 |
| | | Feb-02 | SRM/SPK | 1/3 | 93 | 99 |
| | | May-02 | SRM/SPK | 1 | 93 | 91 |
| | | May-02 | SRM/SPK | 1/3 | 96 | 93 |
| | | | | | | |

| Table 2. (con't.) Standard Reference Material and Spike Recovery Data, May 2001 through May 2002 | | | | | | |
|---|---|---|---|---|---|---|
| **Parameter** | **Lab** | **Cruise Date** | **QC Type** | **Sub-samp** | **% SRM Recovery** | **% Spike Recovery** |
| **TP** | DHMH | May-01 | SPK | 1 | - | 99% |
| | | Aug-01 | SPK | 1 | - | 100 |
| | | Nov-01 | SPK | 1 | - | 98 |
| | | Feb-02 | SPK | 1 | - | 81 |
| | | May-02 | SRM/SPK | 1 | 124% | 95 |
| | | | | | | |
| **PO4** | CBL | May-01 | SRM/SPK | 1 | 104 | 106 |
| | | May-01 | SRM | 3 | 97 | - |
| | | Aug-01 | SRM/SPK | 1 | 101 | 119 |
| | | Aug-01 | SRM | 3 | 91 | - |
| | | Nov-01 | SRM/SPK | 4 | 98 | 104 |
| | | Nov-01 | SRM/SPK | 2 | 91 | 98 |
| | | Feb-02 | SRM/SPK | 1 | 104 | 107 |
| | | Feb-02 | SRM/SPK | 4 | 111 | 108 |
| | | May-02 | SRM/SPK | 1 | 104 | 107 |
| | | May-02 | SRM/SPK | 4 | 111 | 108 |
| **PO4** | ODU | May-01 | SRM | 1 | 92 | 87 |
| | | May-01 | SRM | 1 | 95 | 87 |
| | | Aug-01 | SRM/SPK | 1 | 95 | 93 |
| | | Aug-01 | SRM/SPK | 1/3 | 94 | 95 |
| | | Nov-01 | SRM/SPK | 1 | 95 | 89 |
| | | Nov-01 | SRM/SPK | 1/3 | 96 | 87 |
| | | Feb-02 | SRM/SPK | 1 | 92 | 82 |
| | | Feb-02 | SRM/SPK | 1/3 | 95 | 83 |
| | | May-02 | SRM/SPK | 1 | 100 | 87 |
| | | May-02 | SRM/SPK | 1/3 | 95 | 85 |
| **PO4** | DCLS | May-01 | SRM/SPK | 4 | 90 | 88 |
| | | Aug-01 | SRM/SPK | 1 | 100 | 95 |
| | | Nov-01 | SRM/SPK | 4 | 90 | 90 |
| | | Feb-02 | SRM/SPK | 4 | 100 | 96 |
| | | May-02 | SRM | ? | 100 | - |
| **PO4** | DHMH | May-01 | SPK | 1 | - | 107 |
| | | Aug-01 | SPK | 1 | - | 97 |
| | | Nov-01 | SPK | 1 | - | 91 |
| | | Feb-02 | SPK | 1 | - | 92 |
| | | May-02 | SRM/SPK | 1 | 93 | 93 |

| Table 2. (con't.) Standard Reference Material and Spike Recovery Data, May 2001 through May 2002 | | | | | | |
|---|---|---|---|---|---|---|
| **Parameter** | **Lab** | **Cruise Date** | **QC Type** | **Sub-samp** | **% SRM Recovery** | **% Spike Recovery** |
| **PP** | CBL | May-01 | SPK | 1 | - | 102 |
| | | May-01 | SPK | 3 | - | 95 |
| | | Aug-01 | SPK | 1 | - | 100 |
| | | Aug-01 | SPK | 4 | - | 100 |
| | | May-02 | SPK | 3 | - | 98 |
| **PP** | ODU | May-01 | SRM/SPK | 1 | 106 | 112 |
| | | May-01 | SRM/SPK | 1/3 | 100 | 86 |
| | | Aug-01 | SRM/SPK | 1 | 94 | 99 |
| | | Aug-01 | SRM/SPK | 1/3 | 92 | 101 |
| | | Nov-01 | SRM/SPK | 1 | 99 | 100 |
| | | Nov-01 | SRM/SPK | 1/3 | 95 | 99 |
| | | Feb-02 | SRM/SPK | 1 | 109 | 99 |
| | | Feb-02 | SRM/SPK | 1/3 | 95 | 101 |
| | | May-02 | SRM/SPK | 1 | 100 | 101 |
| | | May-02 | SRM/SPK | 1/3 | 100 | 100 |
| | | | | | | |
| **Si** | CBL | May-01 | SPK | 4 | - | 93 |
| | | May-01 | SPK | 2 | - | 90 |
| | | Aug-01 | SPK | 2 | - | 92 |
| | | Aug-01 | SPK | 4 | - | 95 |
| | | Nov-01 | SPK | 1 | - | 89 |
| | | Nov-01 | SPK | 4 | - | 89 |
| | | Feb-02 | SPK | 2 | - | 89 |
| | | Feb-02 | SPK | 3 | - | 90 |
| | | May-02 | SPK | 1 | - | 94 |
| | | May-02 | SPK | 3 | - | 92 |
| **Si** | ODU | May-01 | SPK | 1 | - | 104 |
| | | May-01 | SPK | 1 | - | 101 |
| | | Aug-01 | SPK | 1 | - | 96 |
| | | Aug-01 | SPK | 1/3 | - | 94 |
| | | Nov-01 | SPK | 1 | - | 98 |
| | | Nov-01 | SPK | 1/3 | - | 98 |
| | | Feb-02 | SPK | 1 | - | 101 |
| | | Feb-02 | SPK | 1/3 | - | 101 |
| | | May-02 | SPK | 1 | - | 103 |
| | | May-02 | SPK | 1/3 | - | 100 |
| **Si** | DCLS | Feb-02 | SRM | ? | 104 | - |
| | | May-02 | SRM | ? | 104 | - |
| **Si** | DHMH | May-01 | SPK | 1 | - | 100 |
| | | Aug-01 | SPK | 1 | - | 95 |
| | | Nov-01 | SPK | 1 | - | ? |



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|---|---|---|---|---|---|---|
| | | May-02 | SRM/SPK | 1 | 100 | 94 |
| | | May-02 | SRM | 1 | 99 | - |